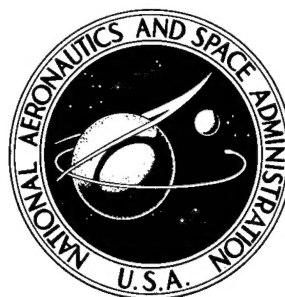


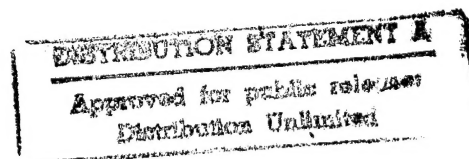
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# PROPERTIES OF SOLID POLYMER ELECTROLYTE FLUOROCARBON FILM

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16. Abstract <p>The ionic fluorocarbon film used as the solid polymer electrolyte in hydrogen/oxygen fuel cells was found to exhibit <u>delamination failures</u>. Polarized light microscopy of as-received film showed a "lined" region at the center of the film thickness. It is shown that these lines were not caused by incomplete saponification but probably resulted from the film extrusion process. (The film lines could be removed by an annealing process.) Chemical, physical, and tensile tests showed that annealing improved or sustained the water contents, spectral properties, thermo-oxidative stability, and tensile properties of the film. The <u>resistivity of the film was significantly decreased by the annealing process.</u></p>			
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# PROPERTIES OF SOLID POLYMER ELECTROLYTE FLUOROCARBON FILM

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## SUMMARY

Studies were made of the delamination and blistering failures of the solid polymer electrolyte (SPE) which occurred during life testing of acidic hydrogen/oxygen fuel cells being developed by the General Electric Company under NASA Johnson Space Center sponsorship. The SPE used was an ionic fluorocarbon film, DuPont R, which after platinization exhibited an unplatinized central region. A similar central lined region was also observed in unplatinized film. It was thought that this lined region at the center of the 0.025-centimeter (10-mil) film thickness was caused by incomplete saponification. However, resistivity and indicator dye studies showed that the film was completely saponified.

Results from X-ray diffraction studies indicated that the central film region was not a region of concentrated polymer crystallinity. Emission spectral data did identify the presence of a wide range of inorganic contaminants.

Annealing of the film showed the lines could be made to disappear. Differential scanning calorimetry data indicated that morphological changes in the polymer accompany the visual loss of the lines during annealing. Thermal gravimetric analysis data showed that annealing the film can be accomplished without affecting its water contents and thermo-oxidative stability. The results from tensile tests showed that annealing of the film does not alter the ultimate tensile strength and the percent elongation. However, the results of resistivity measurements showed that annealing the film significantly decreases the resistivity. Accelerated life testing in prototype fuel cells has shown the annealed film to be as good as the unannealed film with respect to blistering and delamination failure.

## INTRODUCTION

Hydrogen/oxygen fuel cells utilizing solid ionic polymers as the electrolyte are being developed for possible space shuttle application by the General Electric Company under NASA contract NAS9-12332. The polymer film being investigated for use in high-energy fuel cells is the ionic fluorocarbon film known commercially as DuPont R (prior to 1973). The fuel cells are required to provide a service life of at least 5000 hours. A schematic diagram of an acidic hydrogen-oxygen fuel cell assembly is shown in figure 1.

Premature failures of prototype fuel cells have been attributed to delamination and blistering of the solid polymer electrolyte (SPE) down the center of the 0.025-centimeter

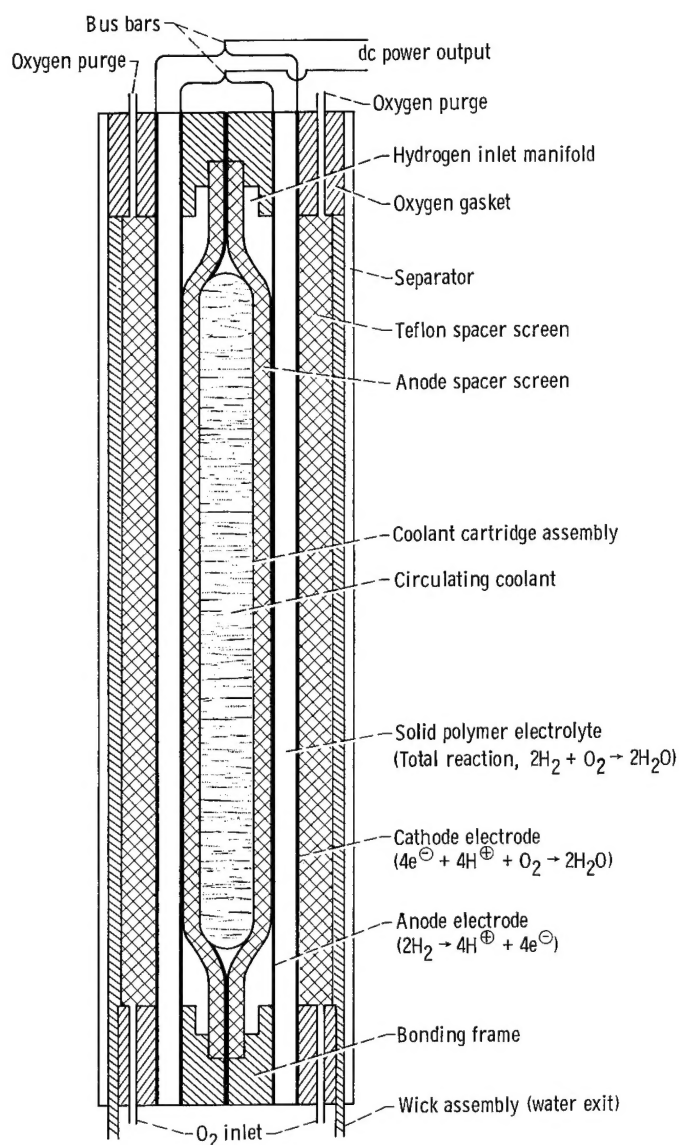


Figure 1. - Schematic of a back-to-back acidic hydrogen/oxygen fuel-cell assembly.

(10-mil) film thickness. Analysis of as-received platinized film by polarized light microscopy showed the presence of a central unplatinized region. This region was thought to result from incomplete saponification during conversion of the nonionic fluorocarbon film to the ionic film version by hydrolysis of the pendant sulfonyl fluoride groups on the fluorocarbon polymer chain. Because the film failures occurred in the central film region, it was postulated that the central unplatinized region is related to the delamination and blistering failure mode of the SPE.

Studies were undertaken at the NASA Lewis Research Center at the request of the NASA Johnson Space Center to provide an insight into the factors which might be responsible for the SPE film failures. The studies reported herein represent the initial phase of an overall effort conducted by several NASA installations to elucidate the failure mechanism for the SPE. This report describes studies that were conducted to evaluate the chemical, physical, and tensile properties of as-received and annealed SPE fluorocarbon film.

Although the International System of Units (SI) is used in the report, the work was done in both the SI and U.S. customary systems.

## MATERIALS AND EXPERIMENTAL PROCEDURE

### Materials

The following types of DuPont R fluorocarbon film were supplied by the contractor, the General Electric Company, Lynn, Massachusetts: (1) unsaponified film (no code number), (2) one-side saponified film (special saponification - no code number), (3) two-side saponified film (code number 11W12A3), and (4) two-side saponified film that was subsequently platinized (no code number).

### Sample Preparation

Water equilibration. - Film samples (2.54 cm by 0.63 cm and 2.54 cm by 2.54 cm) were cut from the three unplatinized types of film and were equilibrated in distilled water at 95° C for 1 hour.

Dye treatment. - Water-equilibrated film samples were immersed at room temperature for 24 hours in each of the following indicator solutions: 0.01 percent aqueous bromophenol blue, 0.01 percent aqueous methyl orange, 0.01 percent aqueous methyl orange - xylene cyanol, and 0.1 percent aqueous methyl orange - xylene cyanol.

## Film Cutting and Mounting

Slide preparation. - The 2.54- by 0.63-centimeter water-equilibrated and dyed film strips were placed between two Teflon blocks so that approximately 0.02 centimeter of the film protruded beyond the edge of one of the blocks. The protruding film was cut with a razor blade by exerting a downward force parallel to the 2.54-centimeter film length. The film was then taped to a glass slide so that the plane of film cross section was parallel to the slide surface. The prepared slides were stored at 25° C in a closed container in which the relative humidity was maintained at greater than 90 percent.

X-ray preparation. - Film strips (2.54 cm by 0.63 cm) were bonded with an epoxy adhesive to one surface of a previously etched Teflon block, as shown schematically in figure 2. A machine bolt with a previously sandblasted head was bonded with an epoxy

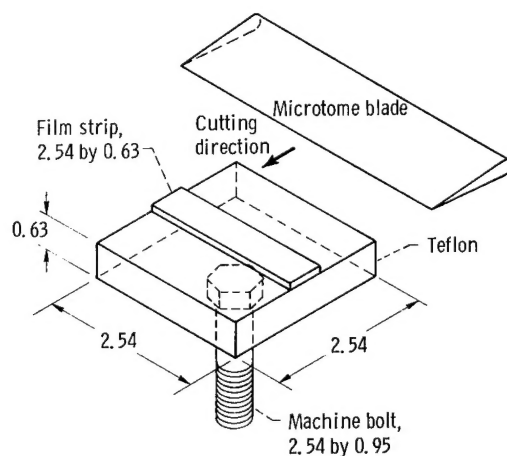


Figure 2. - Schematic of unplatinized film strips and film holder used for microtome cutting. (All dimensions are in cm.)

adhesive to the opposite Teflon block surface. The film strips were then cut into five sections, each 50 micrometers in thickness, by using a manually operated stationary blade microtome set at a cutting angle of approximately 30°. Unsaponified film samples could not be sectioned even at temperatures as low as -20° C because the film would distort as it was lowered past the stationary microtome blade.

## Microscopy

Line viewing. - The mounted film slivers were viewed with a microscope equipped with dual 10X eyepiece lenses, a 1.25X internal lens, an internal polarizer lens, and 5X, 10X, 50X, and 100X objective lenses to give overall magnifications of 62.5X, 125X,

625X, and 1250X. Rotating the object stage or the slide in the field of view (the film itself acts as a polarizer) and lowering the condensor lens below the object stage (and/or adding an extra compensatory condensor lens) allowed the central region film lines to be observed. The lines were most readily observed and best photographed at a magnification of 125X.

Photography. - The microscope was equipped with a Polaroid camera. Polaroid 107 black-and-white film (1- to 3-sec exposure, 15-sec development time) was used to photograph the film lines.

### X-Ray Diffraction Analysis

The transmission Laue technique was used with unfiltered copper K radiation, 3-centimeter distance, and 12-hour exposure to record the X-ray diffraction pattern of the film slivers and microtome sections.

### Emission Spectroscopy

Portions of the film samples were ashed in a heated oxygen atmosphere to burn off the organic material. The concentrated inorganic residue was analyzed qualitatively for the presence of various elements by emission spectroscopy.

### DSC-TGA Analysis

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed under a nitrogen atmosphere at heating rates of 5<sup>o</sup> and 20<sup>o</sup> C per minute, respectively. The percentage of water was calculated from the TGA data.

### Softening Points

A hot-stage, polarized-light-microscopy, melting-point apparatus was used to determine the film softening points and the temperature range for visible loss of the film lines (annealing).

## Heat Treatments

The film samples were placed on a piece of Teflon and heated in an air or nitrogen atmosphere at 235° to 250° C for 0.5 to 2 hours. The films were either fast cooled by quenching in cold water or slow cooled by turning off the oven power and allowing the oven to cool overnight. Vacuum-annealed film samples were prepared in a vacuum oven at 235° to 245° C for 2 hours followed by slow cooling overnight. Autoclave-annealed film samples were prepared by heating samples covered with water in a pressure bomb at 235° to 240° C for 2 hours followed by slow cooling overnight.

## Tensile Properties

The ultimate tensile strength and percent elongation of film samples were determined at room temperature and 50 percent relative humidity with a universal tensile tester. The 1.27- by 7.62-centimeter film samples were held in grips provided with Teflon pads. The gage length used for these tests was 5.08 centimeters. To a strain of 20 percent the load was applied at a speed of 0.25 centimeter per minute. Above 20 percent strain the load was applied at a speed of 2.54 centimeters per minute.

## Conductivity

Aqueous. - Water-equilibrated 2.54- by 2.54-centimeter film samples were placed between two 2.54- by 2.54-centimeter platinized grids equipped with electrical extensions. The assembly was held between two 2.54- by 2.54- by 0.63-centimeter metal blocks by slight hand pressure. An impedance bridge was used to measure the resistivity of the film squares.

Acidic. - Film samples (2.54 cm by 2.54 cm) previously equilibrated in dilute sulfuric acid (pH = 0.96) were measured for electrical resistance with a conductivity cell, as described in reference 1.

## Environment Cycling Tests

The environment cycling tests were performed by Direct Energy Conversion Section, Aircraft Equipment Division of the General Electric Company. Film samples (7.62 cm by 7.62 cm) were mounted in a frame and subjected to a heating, cooling, drying, and humidifying cycling environment until blistering and/or delamination failure resulted.

## RESULTS AND DISCUSSION

DuPont R film is believed to be a copolymer of tetrafluoroethylene and a perfluoro monomer of unknown structure (possibly a perfluoro isopropyl sulfonyl fluoride vinyl ether). The copolymer is fluorinated with elemental fluorine at approximately 100° C to consume residual unsaturation,  $-\text{CF}_2\text{H}$ ,  $-\text{COF}$ , and other impurity groups; however, approximately 10 percent of the impurity groups survive the fluorination step. The copolymer is then extruded at approximately 265° C to obtain a 0.025-centimeter (10-mil) thick film. The film is then believed to be saponified (hydrolyzed) by immersing it in 15 percent aqueous sodium hydroxide at 95° C for 4 hours. The sulfonic acid sodium salts are subsequently converted to sulfonic acids by treatment with an inorganic acid. For fuel-cell uses, the film is then platinized by equilibration with a solution of platinum salts and subsequently reduced to metallic platinum. The center line observed initially in the two-side saponified film (film saponified and acidified as previously described) was thought to result from incomplete saponification of the sulfonyl fluorides in the center of the film. If true, the central region of the film would then possess different optical properties than the remainder of the film, and a line would appear when the film was viewed with a polarized light microscope. Unsaponified film (nonionic film) that has been treated with base and subsequently acidified is hereinafter called saponified film (ionic film).

### Film Curvature

During the water equilibration of the film strips, it was observed that all three samples (unsaponified, one- and two-side saponified films) exhibited some curvature which was retained after they were dried at 25° C in air. The more flexible unsaponified film did not exhibit nearly as much curvature as the saponified films because of the lower intermolecular cohesive forces of attraction. The direction of the film curvature was parallel to the lines on the surface of the film. These lines are believed to be formed during the film extrusion process. Because the saponified water-equilibrated film possesses considerable extensibility (discussed in a following section), the propensity of the film to curve is not considered to be a significant factor in the fuel-cell membrane failures.

### Central Lines

Figure 3 shows a photomicrograph of a cross section of a platinized film membrane. The lines visible in the platinized film are also observed in unplatinized films.

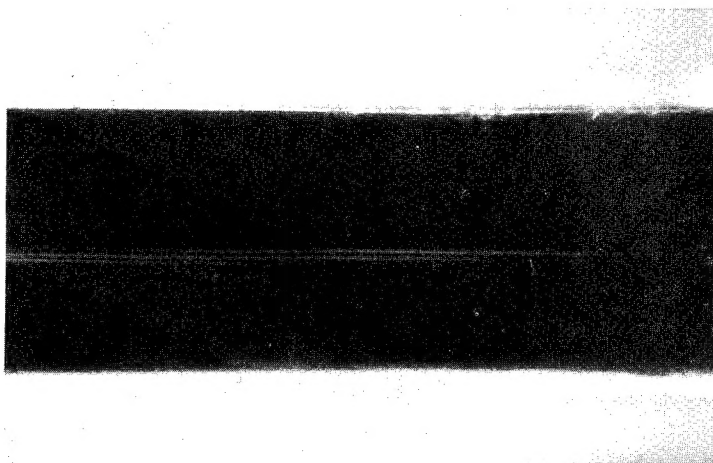


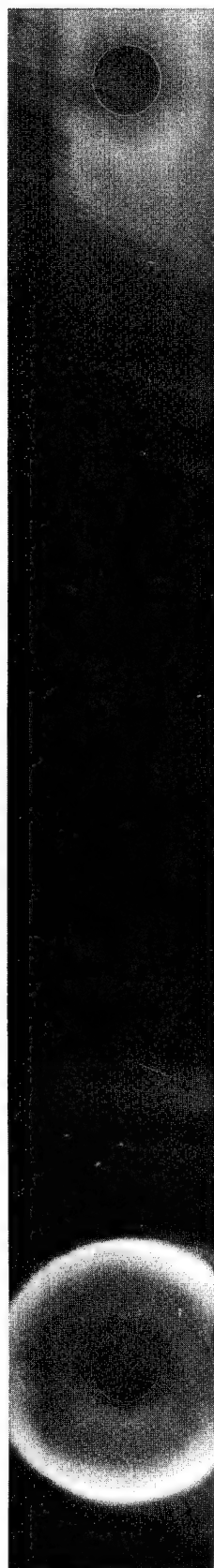
Figure 3. - Cross section of as-received platinized film membrane.

Examples of unsaponified film, one-side saponified film, and two-side saponified film are shown in figures 4(a) to (c). The lines have been observed as a series of six to eight lines centered evenly alongside a darker center line. The lines are generally restricted to the center one-third of the film thickness. Because the lines have been observed in both saponified and unsaponified films, it follows that the lines do not result from incomplete saponification. Further evidence to support the aforesaid conclusion comes from observation of central lines in fluorinated ethylene propylene (FEP) copolymer film, figure 4(d). The FEP film corresponds to unsaponified DuPont R film because both are unsaponified extruded perfluoro copolymers with tetrafluoroethylene as one of the monomers.

### Dye Treatment

Organic indicators of the type normally employed in acid-base titrations were used to further investigate the completeness of the saponification reaction. If the saponification reaction were incomplete, these film regions would be expected to exhibit the indicator color corresponding to pH of approximately 7, while the saponified/acidified film regions would exhibit a color corresponding to the acidic pH of sulfonic acid groups.

Upon treating the films with indicators, the unsaponified film remained colorless while the one- and two-side saponified films were yellow in bromophenol blue, red in methyl orange, pink in dilute methyl orange - xylene cyanol, and red in concentrated (0.1 percent) methyl orange - xylene cyanol. Polarized light microscopy of film slivers cut from the dyed films revealed that the films were uniformly colored throughout their thickness. Because the colors observed correspond to acidic pH's and are present



(a) Unsaponified.



(b) One-side saponified.



(c) Two-side saponified.

Figure 6. - Representative X-ray diffraction patterns of as-received unplatinized films.

throughout the film thickness, it can be likewise concluded that incomplete saponification is not the cause of the central film lines.

### Heat Treatment

Because the central film lines were shown to be present before saponification of the film, it was thought that the lines might result from the film extrusion process. This suggested that the morphological features responsible for the lines might be altered by subjecting the film to an annealing process. Table I summarizes the film annealing con-

TABLE I. - UNPLATINIZED FILM ANNEALING CONDITIONS

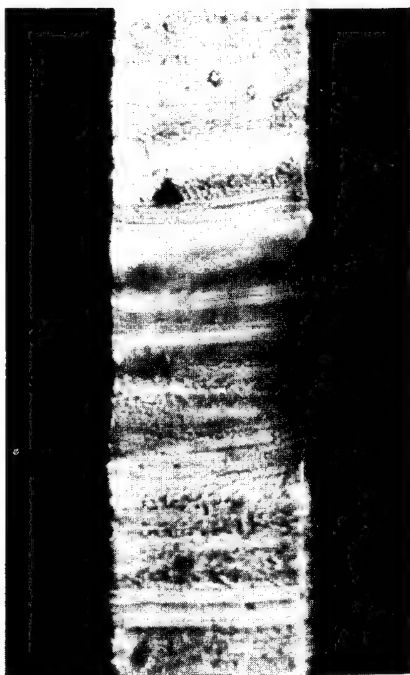
[Annealing time, 0.5 to 2 hr. Cooling rate: fast, quenching in cold water (forced-air oven and nitrogen environments only); slow,  $<1^{\circ}\text{C}$  per minute (all four environments).]

Film type	Environment	Temperature, $^{\circ}\text{C}$
Unsaponified	Forced-air oven Nitrogen Vacuum oven Autoclave (sample under water)	235 to 245
Saponified	Same	195 to 200

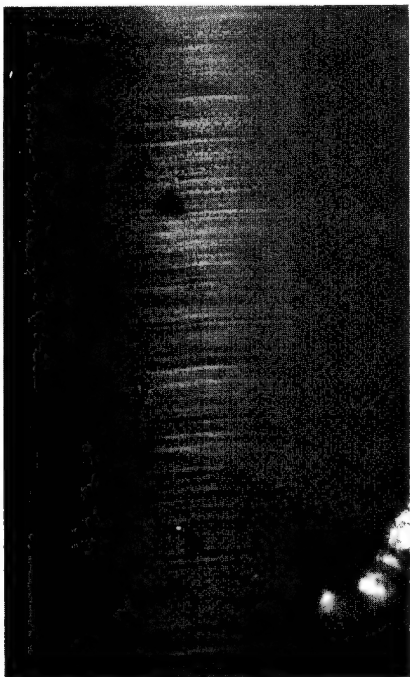
ditions investigated. A photomicrograph of the cross section of each film type that had been heated in air and then quenched in cold distilled water is shown in figure 5. It can be seen in figure 5 that annealing the films did remove or destroy the morphological structures which caused the lines. Similar results were found when the films were annealed in a nitrogen atmosphere, followed by fast or slow cooling. However, heat treatment of saponified films in air, nitrogen, or vacuum caused darkening of the film. The discoloration of the film could be attributed to the thermal decomposition of sulfonic acid groups. Autoclave annealing of saponified films under water resulted in only a slight darkening of the film; however, it was found that unsaponified films could be heat treated in air, nitrogen, vacuum, and autoclave environments without discoloration. To circumvent the darkening problem, unsaponified films were heat treated and subsequently saponified. This procedure was found to produce clear heat-treated films with properties equivalent to or better than commercially available film.

### X-Ray Diffraction Analysis

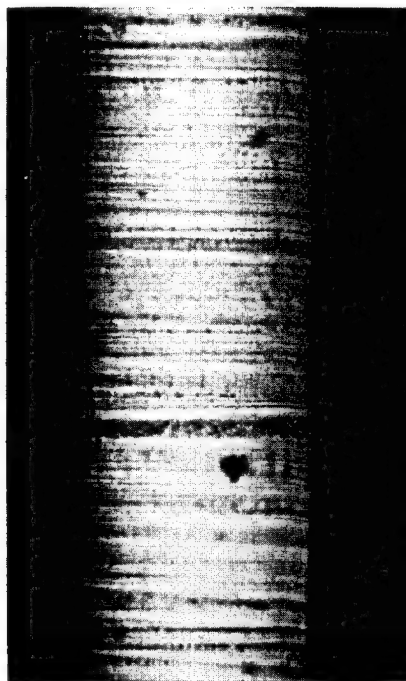
The X-ray diffraction patterns of the entire film thickness of the unsaponified film



(a) Unsaponified.



(b) One-side saponified.

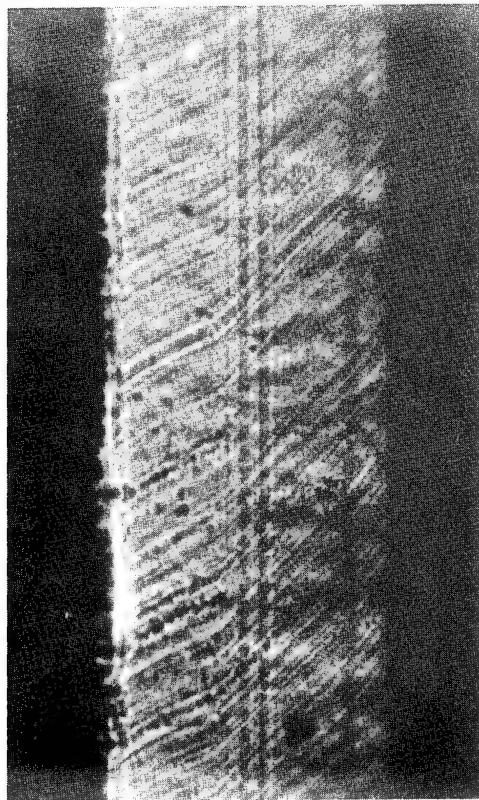


(c) Two-side saponified.

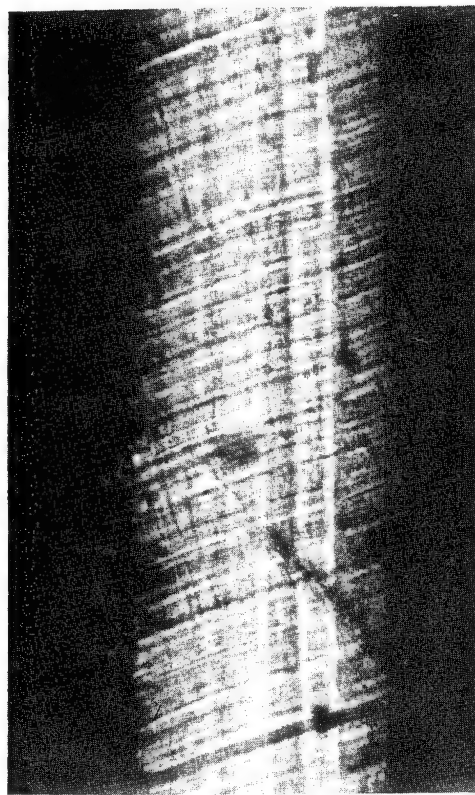
Figure 5. - Cross sections of annealed unplatinized fluorocarbon films.



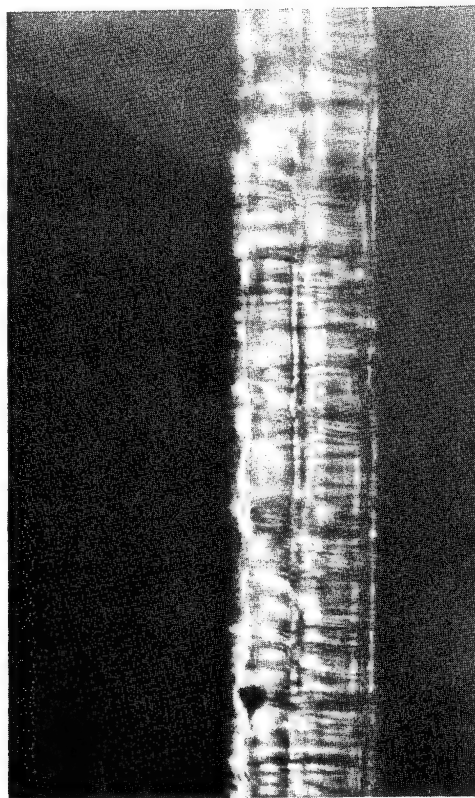
(a) Unsaponified.



(b) One-side saponified.



(c) Two-side saponified.



(d) Fluorinated ethylene propylene (FEP).

Figure 4. - Cross sections of as-received unplatinized fluorocarbon films.

and X-ray diffraction patterns of the entire film thickness and the central 50-micrometer layer of the one- and two-side saponified as-received films and the annealed saponified films were recorded. The X-ray patterns of the central 50-micrometer layer were too low in intensity to permit interpretation. However, the low intensity does suggest that the film crystallinity is uniformly distributed throughout the film thickness rather than being concentrated in the lined central film region.

The X-ray diffraction patterns of the entire film thickness showed the presence of two faint lines in both the unsaponified and one-side saponified commercial films (figs. 6(a) and (b)). However, as can be seen in the figure, the diffuse line patterns were almost obscured by X-ray scattering from the amorphous polymer in the film. The X-ray pattern of the two-side saponified commercial film lacked the diffuse lines, which indicated that the film is quite amorphous (fig. 6(c)). The X-ray diffraction patterns of fast- and slow-cooled unsaponified annealed and saponified annealed films are more diffuse than those of the respective commercial films. This suggests that randomization and diminution of the low level of crystallinity present in the commercial films occurs during annealing of the films. The spacing of the X-ray pattern diffuse lines did not show any significant changes, indicating that the unit cell dimensions were not affected by the film annealing process. The sharp lines observed in some of the X-ray diffraction patterns were measured and compiled into a list of  $d$  A equal to 1.16, 1.22, 1.627, 2.44, 2.851, 3.463, and 3.831. These diffraction line spacings are close to those reported for calcium perchlorate and/or calcium aluminum silicate (a common mineral in nature found in various undefined compositions).

### Emission Spectroscopy

Table II summarizes the emission spectroscopy results. The inorganic impurities suggested by the X-ray results agree with the emission spectroscopy identification of calcium, aluminum, and silicon in the film samples. However, the inorganic impurities

TABLE II. - SUMMARY OF EMISSION SPECTROGRAPHIC ANALYSIS OF  
INORGANIC RESIDUE FROM ASHED UNPLATINIZED

#### FLUOROCARBON FILMS

Elements present equally in unsaponified and saponified film	Elements having increased concentration in saponified film	Elements found randomly in some saponified samples
Ca > Al >> Si > Fe, Cu, Ti, Ni, Zr	Na > B >> Cr, Sn, Zn	K, Co

could be present as compounds other than those suggested by X-ray line spacings. For example, a very strong calcium pattern found for all samples might have resulted from use of a calcium compound, such as calcium fluoride, during monomer synthesis. A strong aluminum pattern and weak-to-very-weak patterns for iron, copper, titanium, and nickel were found for all samples. These patterns could result from residual polymerization catalysts. A medium-strength sodium pattern found in all saponified samples most likely results from the sodium hydroxide used in the saponification process. Faint traces to very weak patterns for chromium, zinc, silicon, tin, zirconium, and boron were found in all samples. Totally random distribution of faint traces of cobalt and potassium was found in a few samples. The total inorganic impurities in any sample comprise less than 1 percent, as shown by the residues left after thermal gravimetric analysis.

### Differential Scanning Calorimetry

Figure 7 shows the DSC results obtained for the three types of unplatinized film in as-received and annealed treatment conditions. The morphological features of the as-received films caused the DSC thermograms to be very complex. Because the DSC thermograms of annealed films are considerably less complex, annealing the films appar -

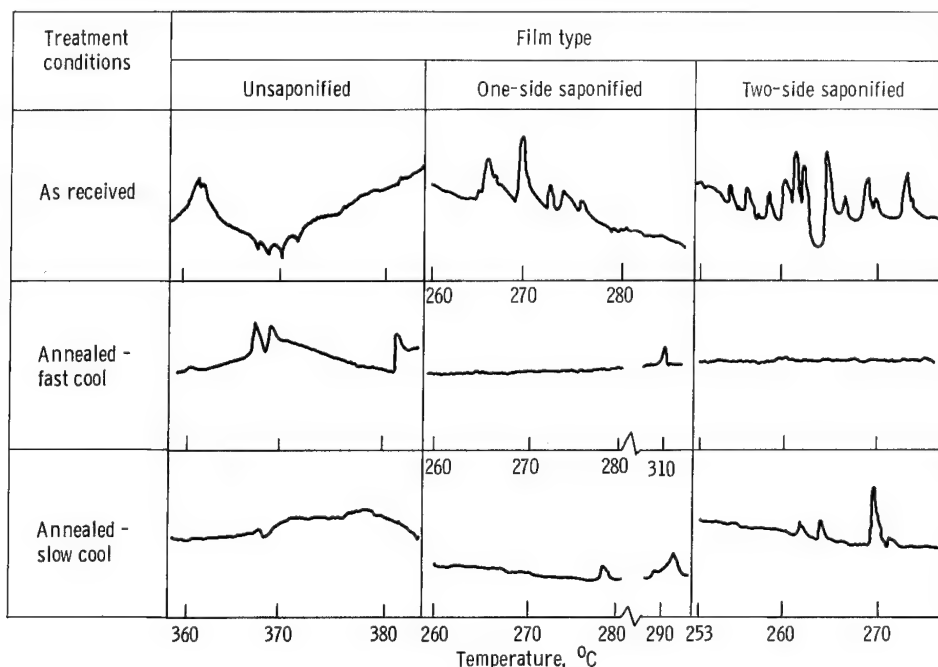


Figure 7. - Differential calorimeter scans of unplatinized fluorocarbon films.

ently altered or destroyed the morphological features responsible for the central film lines. The temperature range at which annealing the films removes the central film lines is approximately  $120^{\circ}\text{C}$  lower for unsaponified films and  $70^{\circ}\text{C}$  lower for saponified films than the temperature ranges shown in figure 7.

The X-ray results obtained by using film sections from as-received film indicated that the central film line region is not a region of concentrated polymer crystallinity. However, annealing may also alter polymer crystallinity in a manner not detected by X-ray analysis. Thus, the changes in the thermograms (within a particular film type) shown in figure 7 could result from changes in polymer crystallinity. Furthermore, the DSC thermograms do not represent glass transition temperature changes because the temperature ranges shown in figure 7 are much higher than the normally low primary and secondary glass transition temperatures of fluoro polymers.

### Thermal Gravimetric Analysis

Figure 8 illustrates representative TGA curves obtained. For the non-water-containing unsaponified films, the rapid weight loss shown in figure 8 suggests that the polymer decomposition mode is that typical of fluorocarbon polymers - a thermal breakdown into volatile segments, including monomers. For the water-containing saponified films, figure 8 illustrates the two types of water in the film: (1) loosely bonded water

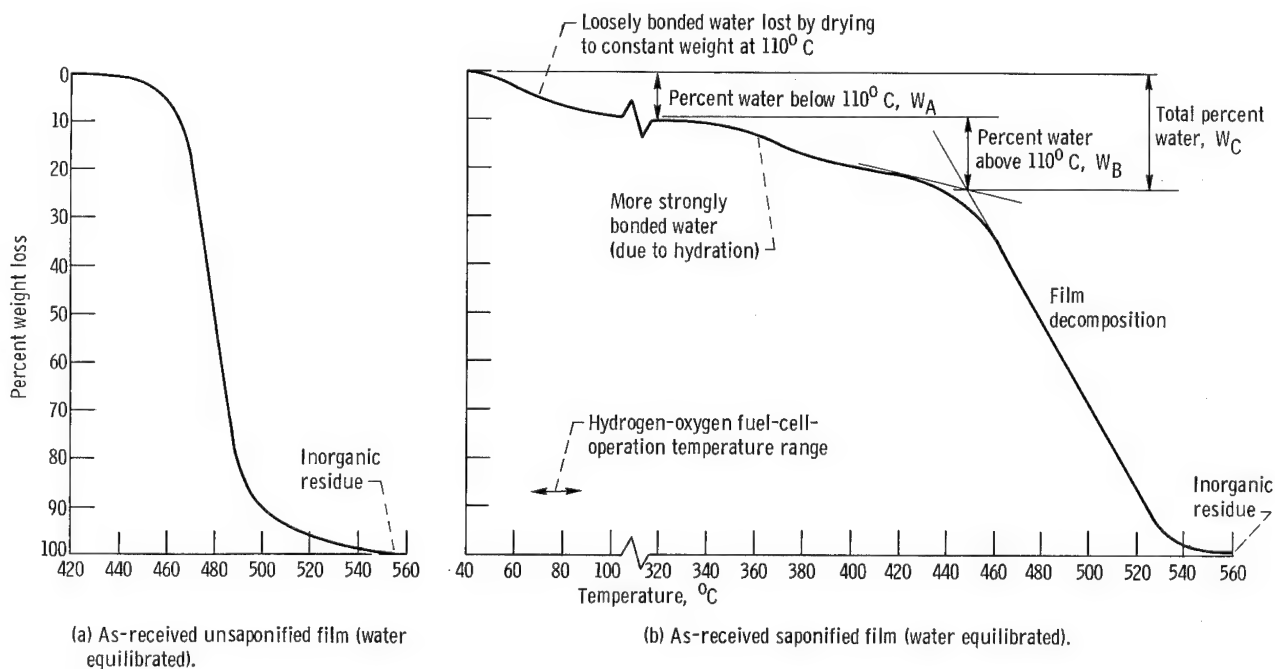


Figure 8. - Representative thermal gravimetric analysis curves of unplatinized water-equilibrated fluorocarbon films.

that is lost by drying to constant weight at 110° C (slightly above normal fuel cell operation temperature) and (2) more strongly bonded water (assumed to be water of hydration on the sulfonic acid groups) that is lost over the temperature range of 320° to 440° C before polymer decomposition becomes significant. Table III summarizes the two types of

TABLE III. - SUMMARY OF UNPLATINIZED FLUOROCARBON FILM WATER CONTENTS

$$[W_A + W_B = W_C.]$$

Film type (water equilibrated)	W <sub>A</sub>			W <sub>B</sub>			W <sub>C</sub>		
	As- received water content, percent	Percent H <sub>2</sub> O below 110 <sup>o</sup> C		As- received water content, percent	Percent H <sub>2</sub> O above 110 <sup>o</sup> C		As- received water content, percent	Total percent H <sub>2</sub> O	
		Annealed			Annealed			Annealed	
		Fast cool	Slow cool		Fast cool	Slow cool		Fast cool	Slow cool
Unsaponified									
As received	1.9	3.1	2.2	0	0.6	0	1.9	3.7	2.2
As received - air dried	0	0	0	0	0	0	0	0	0
Vacuum-oven annealed	----	----	1.2	----	----	----	----	----	1.2
Autoclave annealed	----	----	1.1	----	----	0	----	----	1.1
One-side saponified									
As received	14.0	11.3	8.8	16.3	16.1	17.8	30.3	27.4	26.6
As received - air dried	3.3	3.3	3.0	19.6	29.9	19.6	22.9	24.2	22.6
Two-side saponified									
As received	11.4	11.9	14.1	16.7	17.2	16.5	26.1	27.1	30.6
As received - air dried	1.5	1.7	2.6	19.9	18.7	18.2	21.4	20.4	20.8
Vacuum annealed	----	----	8.8	----	----	4.7	----	----	13.5
Vacuum annealed - air dried	----	----	2.4	----	----	3.8	----	----	6.2
Autoclave annealed	----	----	53.6	----	----	6.8	----	----	60.4
Autoclave annealed - air dried	----	----	26.3	----	----	6.6	----	----	32.9
Annealed unsaponified film (subsequently saponified) <sup>a</sup>									
No annealing (reference)	14.6	----	----	20.2	----	----	34.8	----	----
Air annealing	----	12.8	11.4	----	17.7	15.5	----	30.5	26.9
Vacuum anneal at 220 <sup>o</sup> C	----	----	9.5	----	----	15.0	----	----	24.5
Vacuum anneal at 240 <sup>o</sup> C	----	----	14.8	----	----	17.3	----	----	32.1
Autoclave anneal at 235 <sup>o</sup> C	----	----	20.0	----	----	14.3	----	----	34.3
Autoclave anneal at 250 <sup>o</sup> C	----	----	15.6	----	----	16.8	----	----	32.4
Saponified at 105 <sup>o</sup> C in 20 per- cent NaOH for 7 days (as re- ceived then saponified, or an- nealed then saponified)	12.3	11.4	11.7	16.7	18.0	17.9	29.0	29.4	29.6

<sup>a</sup>Saponified at 95° C in 15 percent NaOH for 2 days.

water in the various films. The equation  $W_A + W_B = W_C$  (where  $W_A$  = percent  $H_2O$  at or below  $110^{\circ}C$ ,  $W_B$  = percent  $H_2O$  above  $110^{\circ}C$ , and  $W_C$  = total percent  $H_2O$ ) represents the three major columns in table III. Variances of as much as  $\pm 2$  percent may be caused by evaporation of film water during the time the films were being wiped dry and weighed before the TGA was begun.

The reason for investigating film water contents was to determine if annealing changed the hygroscopic nature of the films such that the film could be made more resistant to drying out. During fuel-cell operation, drying out of the film occurs by a combination of adverse mass transport phenomena. This drying may contribute to film delamination and blistering. Thus, if annealing films shifts the water available below  $110^{\circ}C$  ( $W_A$ ) to water available above  $110^{\circ}C$  ( $W_B$ ) without altering the total water percent ( $W_C$ ), a fuel-cell membrane more resistant to failure caused by drying out might result. However, comparison of as-received saponified film, with and without annealing, shows that the annealing process did not lessen the tendency of the film to air dry.

The annealing of saponified films in an autoclave or vacuum oven produced total water contents ( $W_C$ ) too far from the desirable 30 percent for suitable fuel-cell usage.

Annealed unsaponified films showed the presence of only traces of water. However, after saponification, these films exhibited total water contents ( $W_C$ ) similar to those of as-received saponified films currently in use. These films have been investigated in accelerated life tests discussed in the section Membrane Testing.

### Tensile Properties

The tensile properties of the various saponified and unsaponified fluorocarbon film types are summarized in table IV. Comparing the results listed in the table leads to the following observations:

- (1) The ultimate tensile strength and elongation of the unsaponified film was not lowered by annealing.
- (2) The as-received one-side and two-side saponified films exhibited ultimate tensile strengths lower than those of unsaponified films. As expected, the elongations of the as-received saponified films were significantly less than those of the unsaponified films.
- (3) Annealing of as-received saponified films did not alter significantly the ultimate tensile strength or elongation.
- (4) The ultimate tensile strength and elongation did not exhibit a dependence on the film directions or cooling rates used in the annealing process.
- (5) Films that were saponified at Lewis for 48 hours in 15 percent sodium hydroxide at  $95^{\circ}C$  had tensile strengths and elongations that compared favorably to those of as-received saponified films.

TABLE IV. - SUMMARY OF UNPLATINIZED FLUOROCARBON FILM TENSILE PROPERTIES  
DETERMINED AT 50 PERCENT RELATIVE HUMIDITY AND 25° C

Sample	Ultimate tensile strength, N/cm <sup>2</sup>		Elongation, percent	
	Parallel <sup>a</sup>	Transverse <sup>a</sup>	Parallel <sup>a</sup>	Transverse <sup>a</sup>
Unsaponified				
As received	3410	3650	434	434
Fast cool	3350	3100	474	463
Slow cool	3440	3280	507	485
One-side saponified				
As received	<sup>b</sup> 2680	<sup>b</sup> 3000	<sup>b</sup> 358	<sup>b</sup> 302
Fast cool	2670	2900	236	235
Slow cool	2820	2650	250	291
Two-side saponified				
As received	<sup>b</sup> 2510	3120	<sup>b</sup> 240	263
Fast cool	3220	2860	233	177
Slow cool	3140	3340	232	238
Annealed unsaponified films (subsequently saponified)				
As received - no anneal	3720	3340	224	178
Saponified at 95° C in 15 percent NaOH for 2 days				
Fast cool	3450	3200	202	182
Slow cool	----	2860	---	131
Saponified at 105° C in 20 percent NaOH for 7 days				
Fast cool	2460	2220	92	166
Slow cool	2460	3040	120	189

<sup>a</sup>Parallel means parallel to surface extrusion lines. Transverse means perpendicular to surface extrusion lines.

<sup>b</sup>Load applied at 0.25 cm/min until failure. For all other samples, load was increased to 2.54 cm/min after 20 percent strain occurred.

(6) The tensile strengths and elongations of films subjected to more severe saponification (105° C, 7 days, 20 percent sodium hydroxide) were somewhat lower than those of as-received saponified films.

### Film Resistivity

The resistivities of the various unsaponified (nonionic) and saponified (ionic) fluorocarbon films in dilute sulfuric acid are given in table V. The resistivities and their changes found for unsaponified films are those commonly displayed by insulating materials. Annealing the as-received saponified films decreased the resistivity by about 20 percent. However, it was previously pointed out that annealing of saponified films also appears to cause decomposition of the pendant sulfonic acid groups. Annealing the as-received unsaponified film and subsequently saponifying for 48 hours in 15 percent sodium hydroxide at 95° C further decreased the resistivity by another 20 percent. Neither of

TABLE V. - SUMMARY OF ROOM-TEMPERATURE RESISTIVITY OF UNPLATINIZED FLUOROCARBON FILM

[Measured in sulfuric acid, pH = 0.96.]

Treatment conditions	Film samples		
	Nonionic, unsaponified	Ionic	
		One-side saponified	Two-side saponified
	Resistivity, ohm-cm		
As-received films			
No annealing	77 000	147	164
Slow cool	980 000	119	113
Fast cool	5 600 000	122	131
Annealed unsaponified films (subsequently saponified) <sup>a</sup>			
No anneal (reference)	-----	---	123
Slow cool	-----	---	92
Fast cool	-----	---	94

<sup>a</sup>Saponified at 95° C in 15 percent NaOH for 2 days.

these decreases in film resistivity can be attributed to an increase in total water content because the water contents of all saponified samples listed in table V are approximately equal (see table III). It is possible that the 48-hour saponification produces a slightly lower resistivity than that of the as-received saponified film. Thus, the entire 40 percent decrease in resistivity might not be caused entirely by annealing of the film. Prolonged saponification of the annealed unsaponified (subsequently saponified) films did not further lower the resistivity reported in table V but did lower tensile properties, as reported in table IV. Similar resistivity results were obtained when the films were measured in a distilled water environment rather than in a dilute sulfuric acid environment. All these results indicate that the use of annealed unsaponified (subsequently saponified) films as the membrane in hydrogen/oxygen fuel cells should lead to an increased electrical efficiency per cell. Thus, fuel-cell assemblies could be designed with more electrical output from fewer cells - an important factor where weight and size are critical.

#### Membrane Testing

The annealed (vacuum oven and air oven) unsaponified (subsequently saponified) films were evaluated by the General Electric Company in their accelerated testing apparatus.

The results of these single sample tests indicated that annealed membranes could be forced to fail and thus do not possess improved resistance to delamination and blistering film failure. However, it must be emphasized that the accelerated test used by General Electric, in which the normal membrane life is compressed by approximately a 50-fold time factor, might be inadequate for detecting improvements in and sustained electrical output under actual long-term usage.

## CONCLUSIONS

Chemical, physical, and tensile tests were made of an ionic fluorocarbon film, DuPont R, used as the solid polymer electrolyte in hydrogen/oxygen fuel cells. Based on the results of this investigation the following conclusions can be drawn:

1. The lines in the central region of the film are not the result of incomplete saponification during film manufacture.
2. The origin of the central film lines is probably the extrusion process used to manufacture the film.
3. The central film lines can be made to disappear by an annealing process.
4. The central film lines are probably not related to the delamination-blistering failure mode because annealed films without lines could be forced to fail in accelerated life testing.
5. The film annealing process does not significantly affect the chemical, physical, and tensile properties of the film. The resistivity of the film was decreased as much as 40 percent by the annealing of unsaponified film and subsequent saponification.

## RECOMMENDATION

To establish if annealed films offer improved life and/or sustained electrical output, a full 5000-hour -life hydrogen/oxygen fuel-cell test is recommended.

Lewis Research Center,  
National Aeronautics and Space Administration,  
and  
U.S. Army Air Mobility R&D Laboratory,  
Cleveland, Ohio, August 7, 1973,  
502-25.

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